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ABUNDANCE AND ELEMENTAL COMPOSITION OF PARTICULATE MATTER IN THE UPPER LAYER OF NORTHEASTERN MEDITERRANEAN

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ABSTRACT

Suspended particulate (POC, PON, PP) profiles obtained in 1991-1994 indicate the existence of characteristic subsurface maxima near the base of the euphotic zone in the cyclonic Rhodes gyre and its peripherial waters in the Northeastern Mediterranean. Interestingly the N:P of the bulk seston was reasonable during stratification seasons when the surface water was relatively poor in phosphate; but the ratio was unexpectedly low (N:P=6-12) in the late winter of 1992 when the surface layer of Rhodes gyre was occupied with nutrient rich deep waters.

1. INTRODUCTION

The eastern Mediterranean is one of the well known region of low productivity over the world due to limited nutrient supply to its surface layer from external and internal sources [1, 2]. The annual rate of phytoplankton production in the basin shows regional fluctuations and has been estimated to range regionally between 16 and 65 gCm^{-2}. The seasonality and the magnitude of primary productivity are principally determined by the extent and duration of winter mixing which provides nutrient inputs from intermediate layers to the euphotic zone [3, 4, 5]. Chlorophyll-a (CHL) concentrations, as a simple but rough measure of phytoplankton biomass, range from 0.01-0.6 μgL^{-1} in summer to 0.1-1.7 μgL^{-1} during the late winter-early spring bloom period [5]. A well-developed deep chlorophyll maximum (DCM) near the base of the euphotic zone is a characteristic feature of the NE Mediterranean throughout almost the whole year [3, 4, 6, 7, 8, 9, 10, 11, 12, 13]. Nevertheless this prominent feature may disappear under severe winter conditions, as experienced in the late winters of 1989 [3, 11] and 1992 [5].

Not unexpectedly, particulate organic matter (seston) content of the eastern Mediterranean surface water is relatively less than in the western basin [9, 14]. During spring-autumn period, when the surface layer is thermally stratified, background seston

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concentrations of the productive upper layer are principally sustained by the regenerated production. Therefore, non-living particles (detritus) constitute a substantial fraction of the bulk seston content of the euphotic zone [15], as occurred in other oligotrophic seas [16, 17, 18, 19].

The deep water of the NE Mediterranean is relatively rich in dissolved inorganic nutrients (NO_3=4-6 μM and PO_4=0.15-0.22 μM) but with a relatively high N:P ratio (=26-28) [4] compared to the deep oceanic values (=14-17) [20]. Therefore, nutrient inputs from the deep layer to the surface waters by advective and convective mixing in winter occur with the indicated high ratios [3]. This process most probably leads to phosphorus-limited algal growth in the euphotic zone of the eastern Mediterranean [21, 22]. Moreover, the limited nutrient supply from the deep waters with relatively high N:P ratios is expected to affect the chemical composition of biogenic particles synthesized in the euphotic zone. Unfortunately, no systematic data is available for a sound understanding of seasonal and spatial variability in both the abundance and elemental composition of seston in the northeastern Mediterranean. For this goal, seston samples were collected from the upper layer of the NE Mediterranean in 1991-1994 period, in the scope of the ongoing national oceanographic program. Particulate organic carbon, nitrogen and total particulate phosphorus concentrations of the seston retained on filters have been evaluated on the seasonal and regional basis, together with the hydrographic, optical, chlorophyll and dissolved inorganic nutrient data from the same sites.

2. METHODOLOGY

Oceanographic data discussed in this article were obtained during the October-91, March-92, July-93 and March-94 cruises in the NE Mediterranean. The October-91 and July-93 surveys represent the period of seasonal stratification in the surface waters whilst the March data stand for the late winter-early spring conditions. Unfortunately, no data was obtained in summer 1992 and winter 1993. The study area and the positions of sampling stations, located between the longitudes 28°00′-36°00′ E and latitudes 34°00′-36°45′ N, are shown in Figures 1 and 2, respectively.

Water samples for chemical measurements were collected with 5L-Niskin bottles on a Rosette attached to the Sea-Bird CTD probe down to 1000 m. The upper layer from surface to below 1% light depth were sampled for particulate organic carbon (POC), nitrogen (PON), particulate phosphorus (PP) and chlorophyll-a (CHL) analyses. Particulates retained on GF/F filter pads for POC and PON analysis were determined by the conventional dry combustion technique [23], using a Carlo Erba model 1108 CHN analyzer. PP content of the seston was determined by the method of dry combustion + colorimetric measurement [24]. CHL samples, homogenized and extracted into 90% acetone solution, were measured by the standard fluorometric method [25], using a Hitachi F-3000 Model fluorometer and a commercially available CHL standard (Sigma).

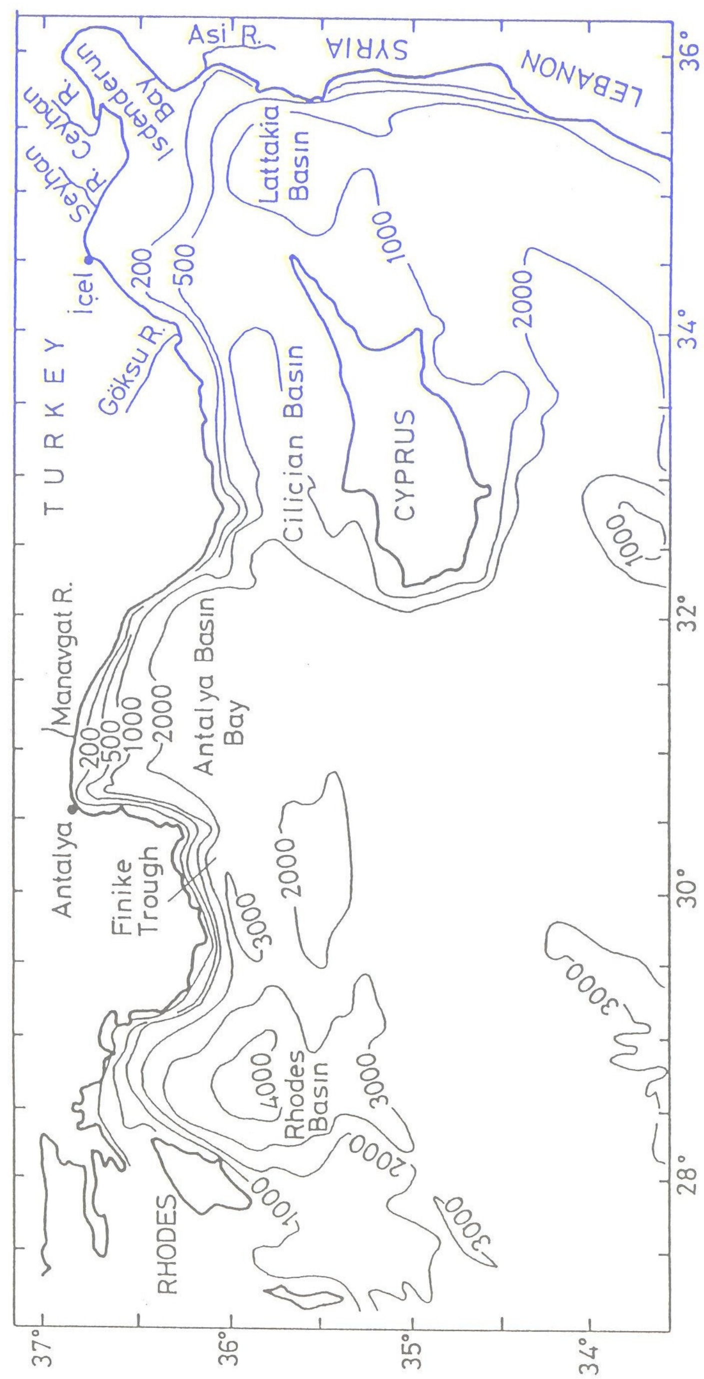

Figure 1. Location map and bathymetry of the NE Mediterranean with the nomenclature of major sub-basins

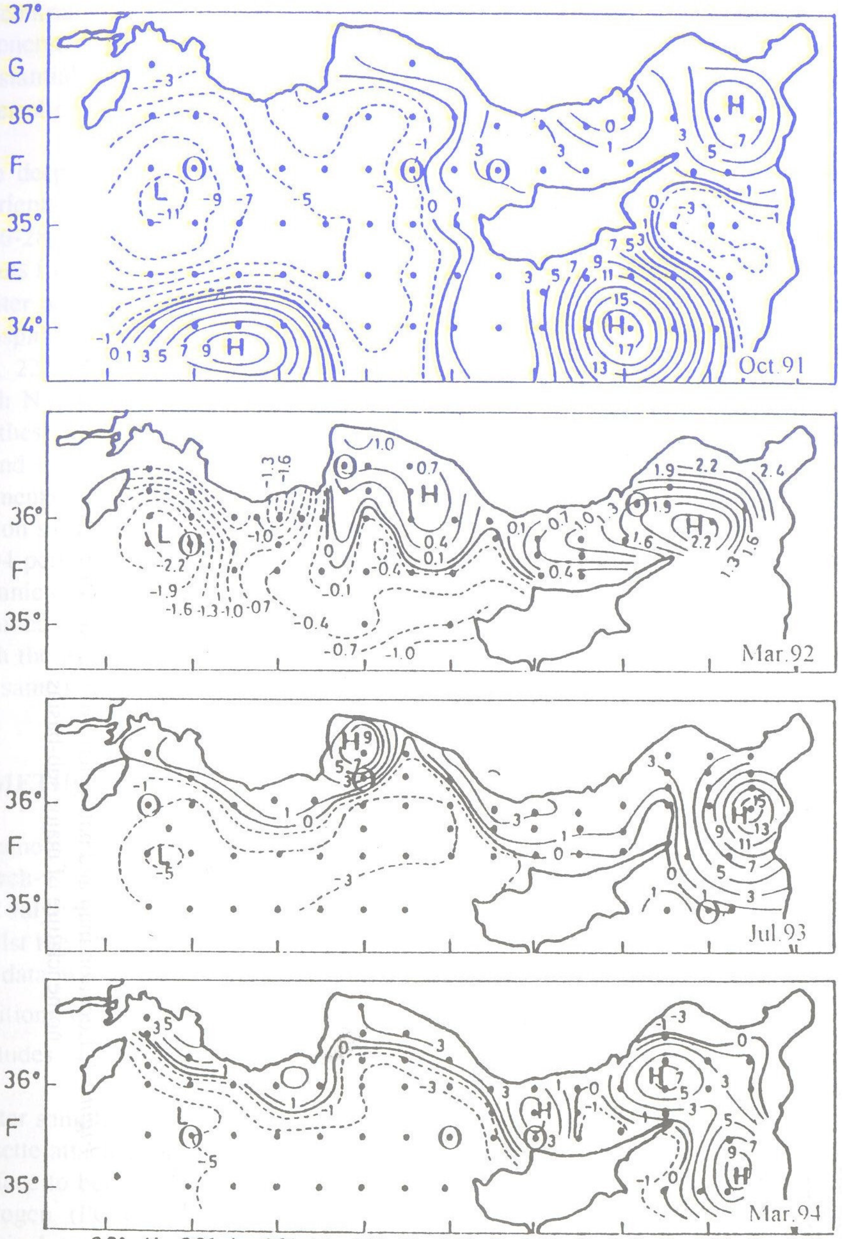

Figure 2. The surface geopotential height anomalies and locations of stations during Oct-91, Mar-92 (modified from Sur et al., 1993), Jul-93 and Mar-94 (unpublished data). Dynamic topography contours are given in centimeter units and L and H show low (cyclonic) and high (anticyclonic) pressure areas.

Seawater samples for NO_3+NO_2 and PO_4 were put into 50 mL HDPE bottles and kept frozen until analysis by a Technicon Model two-channel autoanalyser. The analytical methods followed were very similar to those described in [26].

3. RESULTS

3.1. WATER COLUMN STRUCTURE

The hydrodynamics and hydro-chemistry within the NE Mediterranean Sea display three regions of distinct vertical features. They are the cyclonic Rhodes Gyre (L), the Cilician Basin with a quasi-permanent anticyclonic eddy (H) and fronts+peripheries. As clearly shown in Figure 2, the region off Antalya bay is a typical site for fronts and peripheries between the cyclonic and anticyclonic eddy fields.

The hydrographic properties of the NE Mediterranean upper layer in March 1992 were apparently different from the vertical structure in March 1994 (Fig. 3). Prolonged winter conditions in 1992 permitted the deep water to occupy the entire upper layer of the Rhodes cyclonic region. This process resulted in the formation of a markedly thick, well-mixed (isohaline and isothermal) upper layer in March 1992. For example, typical temperature, salinity and density profiles displayed in Figure 3 demonstrate that the Rhodes upper layer was homogenized thoroughly by advection of the deep water and subsequent convective mixing down to at least 1000 m. The isothermal (~13.8 °C) and isohaline (~38.8 ppt) upper layer water possessed slightly higher salinity and temperatures values than the those of the Levantine Deep Water (LDW) determined previously as T=13.6 °C and S=38.7 [27, 28], due to mixing with the warmer and saltier surface waters of the Rhodes region under prolonged winter conditions. However, during the period of seasonal stratification LDW may rise up to 50 m in the Rhodes gyre but merely to 100 m in peripheries and 150 m in the Cilician basin (Fig. 3). In other words, the upper layer of the NE Mediterranean is occupied with saltier and warmer waters (thus less dense), separated from LDW by a pycnocline. This quasi-permanent density gradient zone appeared to be situated at relatively shallower depths (50 m) in the Rhodes cyclone in October 1991 and July 1993 (Fig. 3); it was completely destroyed in the core of the Rhodes cyclone during the winter of 1992 [29], as previously experienced in 1987 [30].

In the upper layer of the Cilician Basin, small scale anticyclonic eddies are generally established [27, 28, 31] with the hydrographic structures apparently different from that of the Rhodes cyclone. In summer-autumn period, the Cilician surface water is more saline and warmer (Fig.3), below which a less saline, cooler water (<39 ppt) of Atlantic origin may be seen until winter mixing. A vertically homogeneous water layer at intermediate depths, overlying the LDW during the period of seasonal stratification in the surface water, is called the Levantine Intermediate Water (LIW) and characterised by a temperature of around 15.5 °C and salinity of 39.1 [27, 32]. The thickness of LIW layer changes seasonally and regionally. In winter, LIW is mixed thoroughly with the salty surface waters to form a vertically homogenous upper layer.

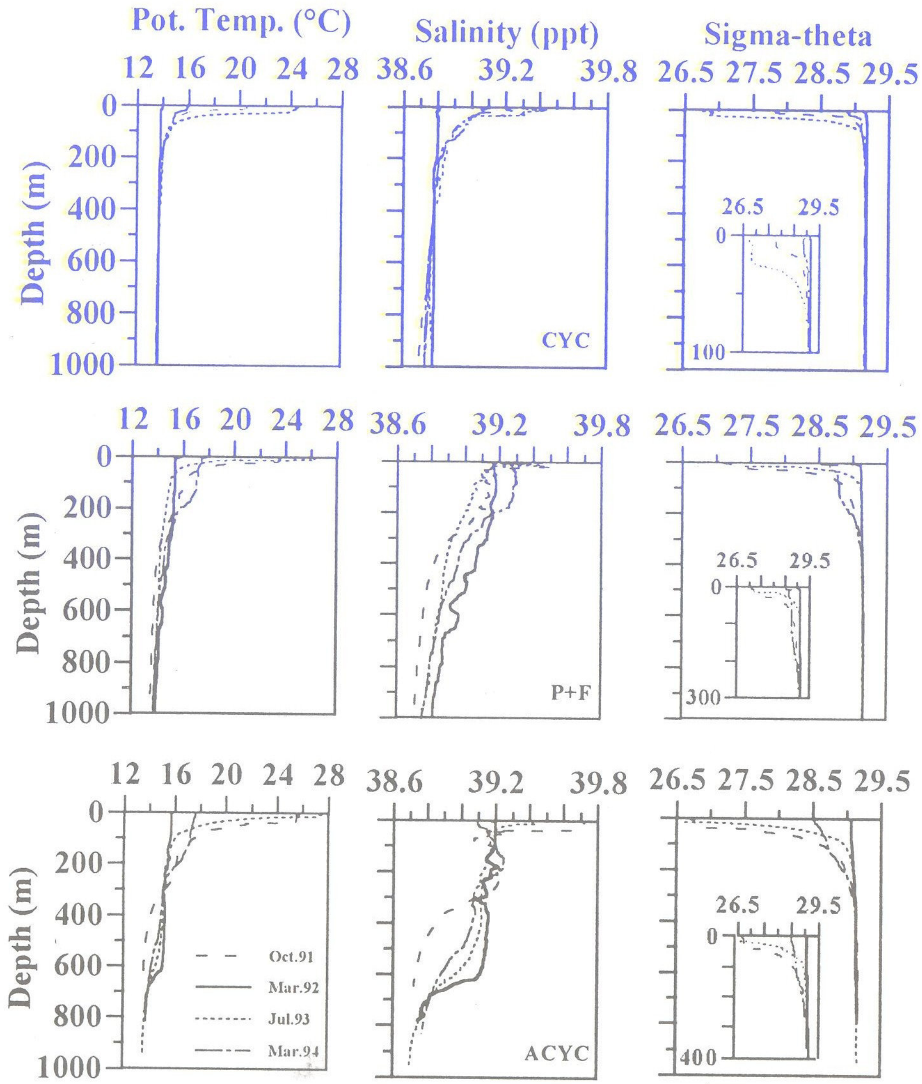

Figure 3. Vertical profiles of hydrographic parameters (after Sur et al., 1993 and unpublished data of the Institute of Marine Marine Sciences, Physical Oceanography Section) for selected stations in the Rhodes Gyre (CYC), Peripherial and Frontal areas (P+F) and Cilician Basin (ACYC) for Oct. 91 - Mar. 94. Station locations are marked in Fig. 2.

As clearly shown in Figure 3, in the frontal zone off the Antalya bay and anticyclonic Cilician region, the upper mixed layer was much thicker (300-600 m) in the winter of 1992 than in the winter of 1994 (200-300 m). A well defined seasonal stratification in the surface water was observed at around 50 m in summer-autumn period (Fig. 3).

3.2. WATER TRANSPARENCY

Measurements of irradiance indicate that 1% of surface light intensity (defining the base of the euphotic zone) penetrates to a depth of 70-110 m in the Cilician basin; it is relatively shallow (45-80 m) in the more productive Rhodes cyclonic and Antalya Bay regions. The present data are consistent with those obtained by [33] who determined the 1% light depth to range between 55 and 95 m, with an average value of 80 m for the whole NE Mediterranean. The 1% light depth measured in this study are also depicted on the CHL profiles for a better understanding of the role of basin hydrodynamics on the biochemical and optical properties of the NE Mediterranean.

The downward attenuation coefficient (K_d) estimated from the measurements of irradiance in the NE Mediterranean in 1991-1994 was found to range from 0.04 m^{-1} in the anticyclonic region during summer-autumn period, to 0.12 m^{-1} in cyclonic and frontal regions during winter-early spring period with an average value of 0.057 m^{-1}.

3.3. NUTRIENTS

Basin-wide, long-term studies conducted since 1988 have shown the critical role of convective mixing and advection of deep water in winter on the spatial and seasonal variations of the nutrients in the upper layer of NE Mediterranean [4, 10]. In the Rhodes cyclonic gyre, the nutrient concentrations of the surface water are closely associated with the hydrographic structure. Simply put, in March 1992 when the upper layer was occupied completely by the LDW with the associated chemical properties, vertically uniform nutrient profiles were obtained throughout the water column down to a depth of about 1000 m (Fig. 4). Nevertheless, the nutrient concentrations of the euphotic zone were very similar to the characteristic values of LDW (PO_4=0.2 μM, NO_3=5.5 μM). In March 1994, the saltier surface water was separated from the LDW by a sharp pycnocline located at 50 m (Fig. 4), indicating less severe winter conditions to be insufficient for the advection of LDW up to the surface layer of the eddy. Thus, nutrient supply to the upper layer from the LDW through the nutricline became very limited; the surface concentrations were measured to as low as about 0.5 μM for NO_3 and 0.02 μM for PO_4 (Fig. 4). The nutricline strictly coincided with the quasi-permanent pycnocline just located near the base of the euphotic zone in the Rhodes cyclone (Fig. 4). The shallow nutricline permits a partial nutrient supply to the lower depths of the euphotic zone, where the light intensity is always a limiting factor for algal growth at such depths.

In the fronts and periphery off Antalya bay, the nutricline appeared to be located at 75-100 m in summer-autumn period, which permits to a limited nutrient supply to the

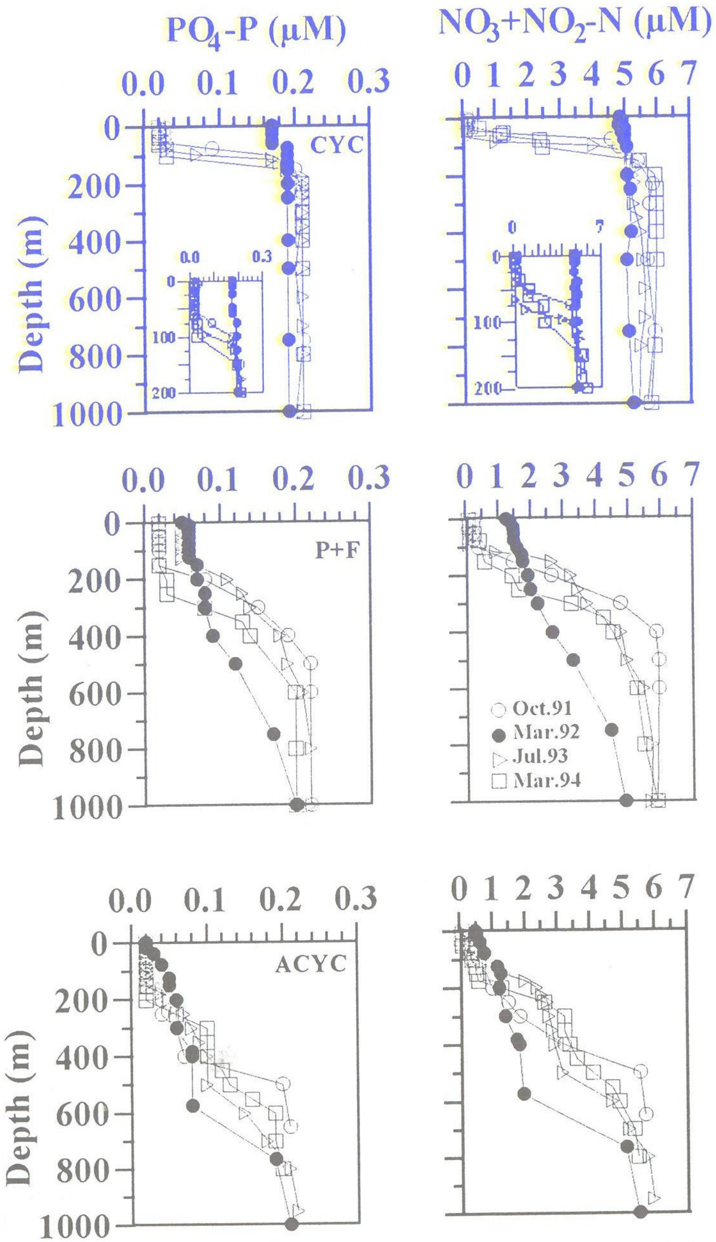

Figure 4. Vertical profiles of dissolved nutrients for selected stations in the Rhodes Gyre (CYC), Peripherial and Frontal areas (P+F) and Cilician Basin (ACYC) for Oct.91 - Mar. 94. Station locations are marked in Fig. 2.

lower depths of the euphotic zone (Fig. 4). Under less severe winter conditions, the nutricline depth is slightly modified, as experienced in March 1994 (Fig. 4). However, during the prolonged winter of 1992, the frontal surface waters appeared to be relatively enriched in nutrients by the supply from the nutricline depths; the euphotic zone concentrations increased from 0.02 µM in summer to the levels of 0.05 µM for PO_4 and from 0.11 µM to 1.5 µM for NO_3. Moreover, the permanent nutricline became broader and moved to a greater depth (500 m) and also the nutrient content of LIW increased apparently in March 1992 relative to those measured in October 1991 (Fig. 4). This supply was provided from LDW through the pycnocline by means of intense convective mixing in winter, which also modified the structure of density gradient between the LIW and LDW (Fig. 3).

In the Cilician basin, where an anticyclonic eddy is formed quasi-permanently, the chemical profiles are also associated with hydrographic structure. As clearly shown in Fig. 4, the saltier surface waters are always poor in nutrients due to establishment of the nutricline at much greater depths than in the Rhodes cyclone. Because the limited nutrient supply from the deeper waters is utilized in photosynthesis the surface concentrations are as low as 0.02 µM for PO_4 and 0.2-0.3 µM for NO_3 throughout most of the year. Below the euphotic zone, there exists a nutrient-poor aphotic layer which explicitly coincides with the LIW layer (Fig. 4). The nutrient-poor LIW layer may extend down to 300-500 m, as experienced in October 1991 and July 1993 (Fig.4), and to greater depths in the southeastern Mediterranean [3]. The nutrient content of LIW remains almost constant with depth down to the permanent nutricline of the anticyclones; but the concentrations slightly increase from spring to autumn until deep winter mixing, due to the supply of particulate nutrients from the surface layer. In winter, the LIW layer is mixed with the surface waters by convective processes, leading to a net export of nutrients to the surface layer. The nutrient-poor LIW does not appear in the cyclonic region (Figs. 3 and 4). The nutricline below the LIW extend down to the boundary of LDW throughout the basin (Figs. 3 and 4). Although its depth and thickness vary in space and time, the upper and lower boundaries of the nutricline are defined by the 29.00-29.05 and the first appearance of the 29.15 density surfaces, as recently reported [4]. In the Cilician basin the nutricline onset appeared at a relatively shallower depth (200 m) in the winter of 1994 than in the summer-autumn period (Fig. 4).

3.4. PARTICULATE ORGANIC MATTER AND CHLOROPHYLL-A IN THE UPPER LAYER OF THE NE MEDITERRANEAN

3.4.1. Rhodes Gyre

Particulate organic carbon, nitrogen and phosphorus concentrations were relatively low in the surface mixed layer of the cyclonic eddy during the summer-autumn period (Fig. 5a). The highest particulate concentrations were consistently recorded at the depth of the DCM (around 60 m), reaching the levels of 3.16 µM for POC, 0.23 µM for PON and 0.026 µM for PP in October 1991, whilst the corresponding maxima for July 1993 being 6.62, 0.57 and 0.036 µM respectively. In March 1994, the vertical distribution of

POM in the euphotic zone appeared to be consistent with that of CHL-a, with less pronounced maxima observed at shallower depths than in the summer-autumn period. Under the prolonged winter condition of 1992, the Levantine deep waters with their associated chemical properties occupied the surface layer. Efficient convective mixing in the upper layer led to the formation of vertically uniform POM and CHL-a profiles in the core of the gyre (Figs. 5a and 6). Although the entire upper layer of the Rhodes cyclonic region was occupied with the relatively nutrient-rich deep water in March 1992, the highest concentrations of both POM and CHL-a were recorded in the frontal areas off Antalya bay (Fig. 5b and 6) as discussed below.

3.4.2. Frontal area between the Rhodes eddy and Antalya basin

Fig. 2 shows the sampling location in March 1992 where the saltier upper layer of the studied site was partly diluted with the deep water by convective mixing down to about 400 m. Consequently, the upper layer was enriched to some extend with dissolved inorganic nutrients as clearly shown in Fig 4. In the region coherent subsurface particulate peaks for March 1992 were recorded at 30-40 m (Fig. 5b) whilst the CHL-a distribution was nearly uniform over the entire euphotic zone with a small increase at the 1 % light depth (Fig. 6). Interestingly, primary productivity measurements at the same location indicated the maximum carbon uptake rate to occur at 35 m [33], coinciding with the particulate maxima and corresponding to the depth of 10 % of the surface irradiance (Fig. 6). In March 1994 when the convective mixing was relatively weak, the subsurface peaks of POC and PON profiles were coincident with the relatively broad DCM established between 40-80 m. On the contrary, the PP profile displayed a slightly increasing trend below 50 m and then retained almost constant down to 90 m, where POC and PON dropped to minimal values. In July 1993, the pronounced particulate maxima well coincided with the DCM formed between 65 and 75 m. Moreover, the POM and CHL-a maxima were as high as those obtained in March 1994. On the other hand, POC and PON data from October 1991 displayed insignificant variation with depth in the upper 150 m. The concentrations obtained below 80 m were similar to July-93 data. At this station the Oct-91 surface CHL-a values were as low as 0.01 μgL^{-1} and comparable with the July 1993 measurements. The Oct-91 CHL-a profile displayed a weak and broad peak between 60-120 m whilst the July 1993 peak was formed between 60-80 m.

3.4.3. Cilician Basin

An anticyclonic eddy is formed quasi-permanently in the region (Fig. 2). In March 1992 particulate and CHL-a data displayed vertically almost similar distributions in the euphotic zone; the concentrations of POC and PON decreased slightly at 30-50 m (Fig. 5c) whilst the CHL-a profile displayed a similar subsurface minimum but at shallower depths (20-30m) (Fig. 6) relative to the depth of the particulate minimum. At the base of the euphotic zone an increase was observed in the POC and PON profiles, where the CHL profile displayed a contrary view decreasing markedly from 0.28 μgL^{-1} at the surface to 0.14 μgL^{-1} at 80 m. Interestingly, the March-92 particulate concentrations were less than or comparable with the October-91 and July-93 values (Fig. 5c) whilst the corresponding CHL-a data displayed an opposite trend in the first 80 m (Fig. 6).

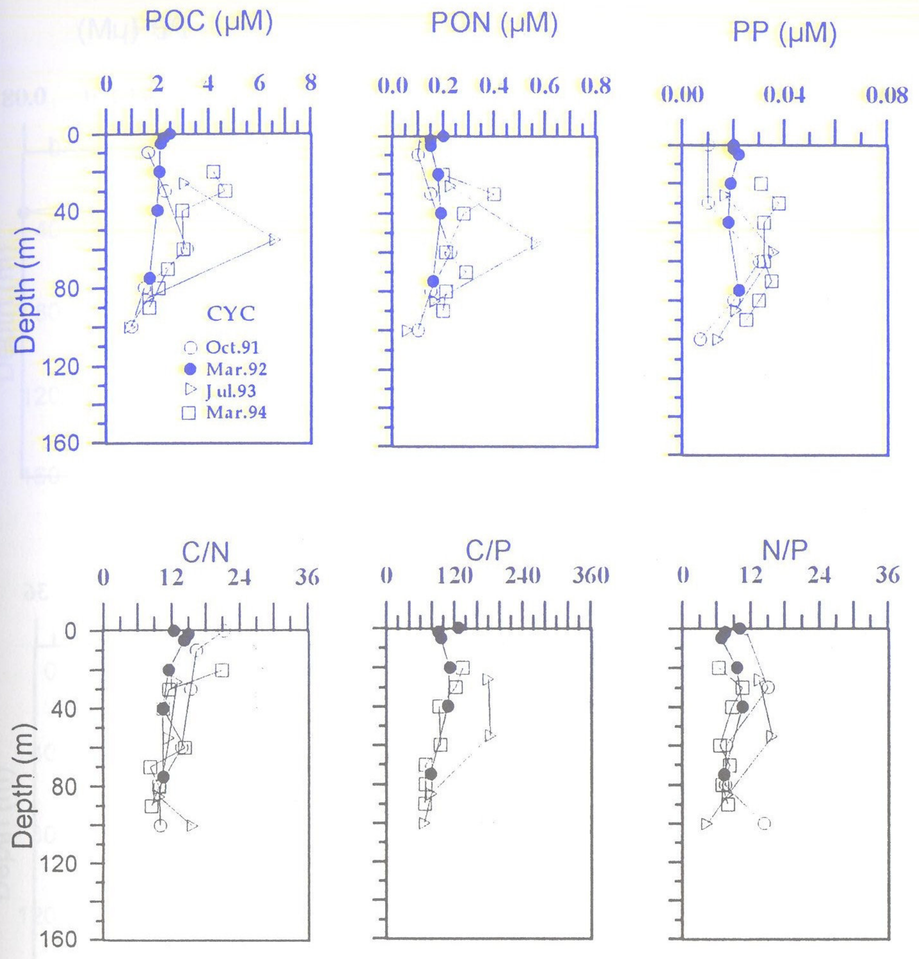

Figure 5a. Vertical profiles of POC, PON and PP and elemental ratios for selected stations in the Rhodes Gyre (CYC) for Oct.91 - Mar.94. Station locations are marked in Fig. 2.

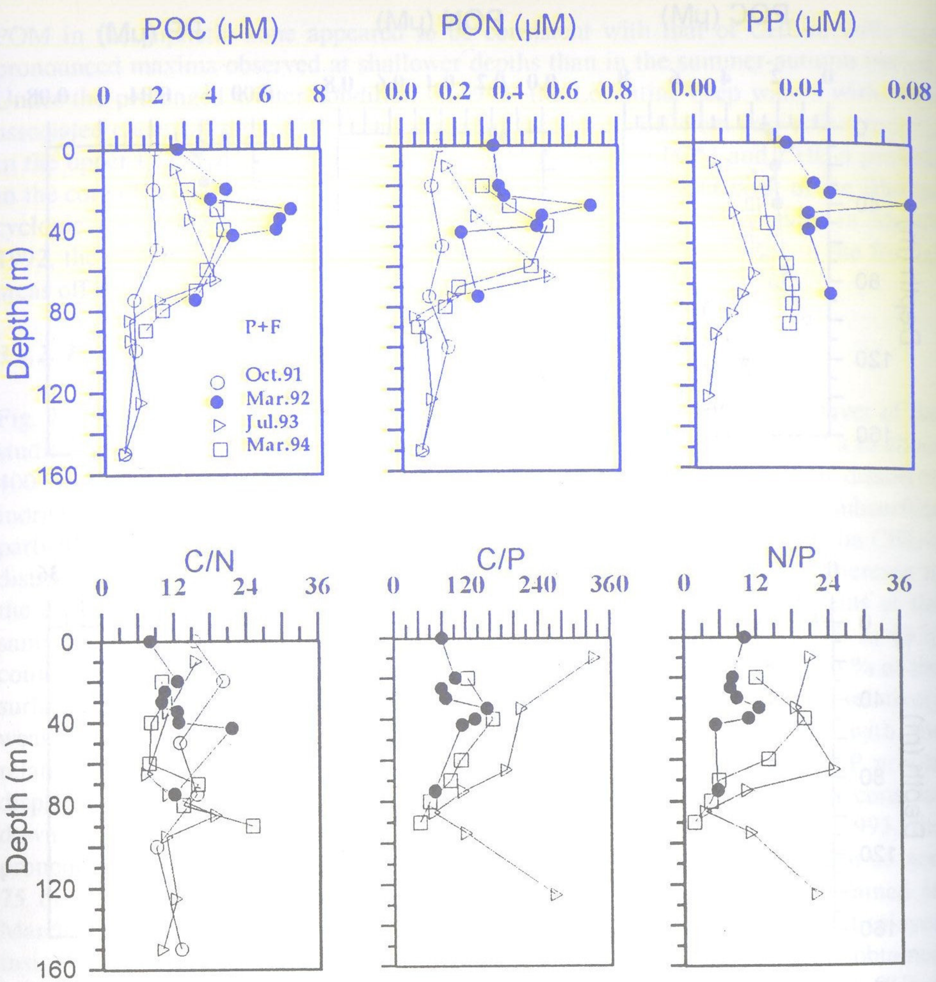

Figure 5b. Vertical profiles of POC, PON and PP and elemental ratios for selected stations in the Peripherial and Frontal areas (P+F) for Oct.91 - Mar.94. Station locations are marked in Fig. 2.

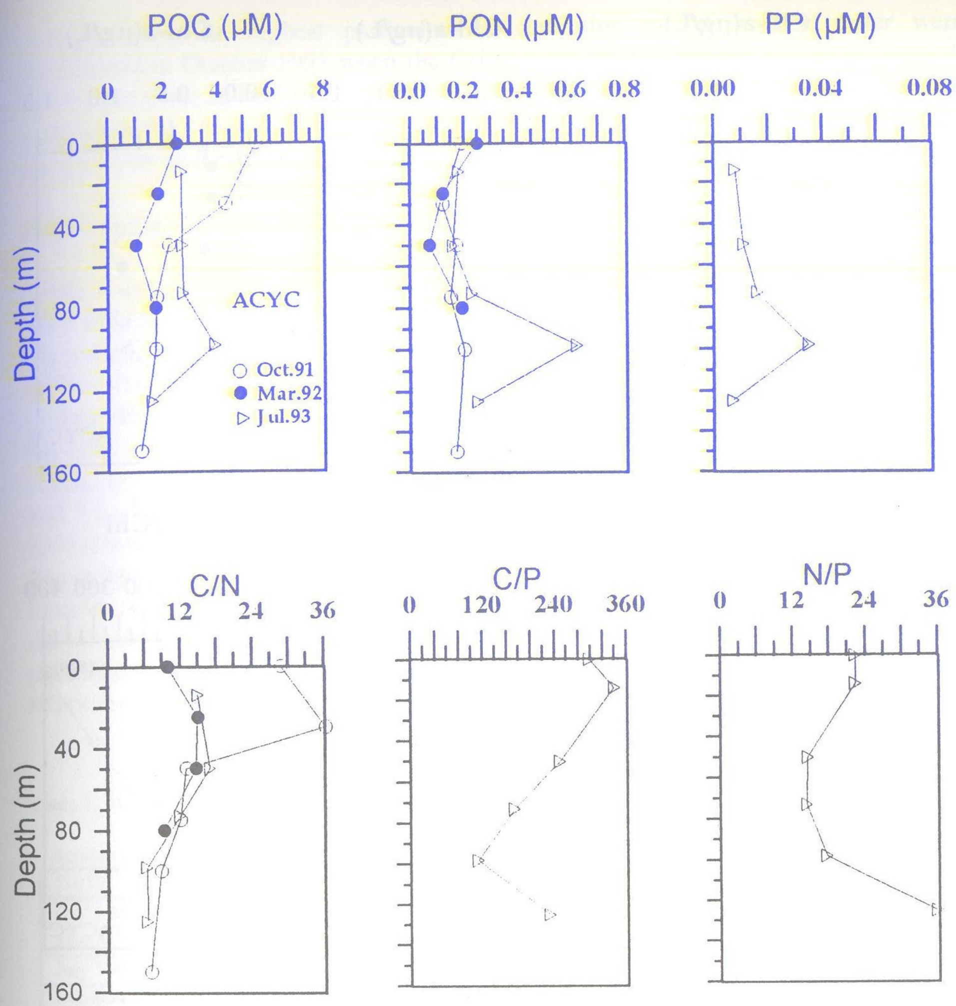

Figure 5c. Vertical profiles of POC, PON and PP and elemental ratios for selected stations in the Cilician Basin (ACYC) for Oct.91 - Mar.94. Station locations are marked in Fig. 2.

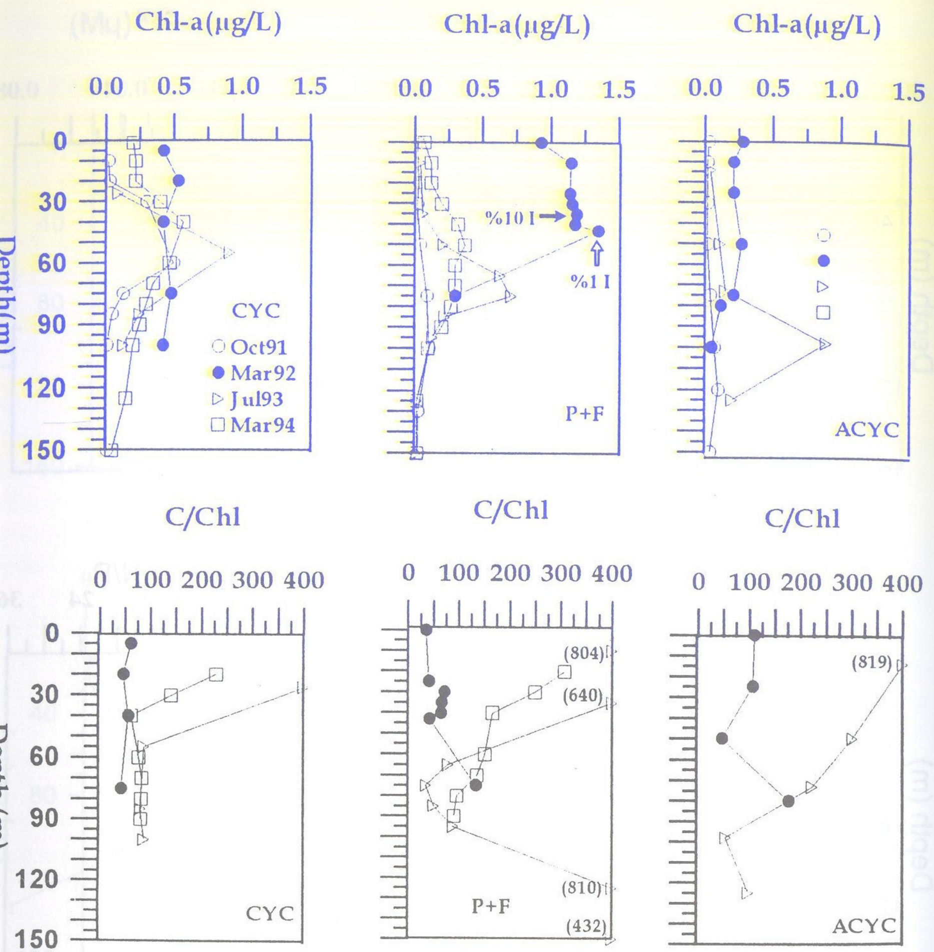

Figure 6: Vertical profiles of CHL-a and C/CHL ratios for selected stations in the Rhodes Gyre (CYC), Peripherial and Frontal areas (P+F) and Cilician Basin (ACYC) for Oct.91 - Mar.94. Station locations are marked in Fig. 2.

Unexpectedly, the highest particulate concentration in the surface water were determined in October 1991 when the CHL content of the euphotic zone being much lower than those of July 1993 and March 1992 (Figs. 5c, 6). The July 1993 particulate profiles in Fig. 5c demonstrate well defined subsurface maxima which coincide with the DCM formed at 100 m, nearly corresponding to the base of the euphotic zone.

3.4.4. Average particulate concentrations

Table 1 shows depth-averaged concentrations of POC, PON and PP for the euphotic zone of hydrodynamically different regions of the NE Mediterranean. It appears that the seasonality in POC and PON content of the cyclonic Rhodes region is higher than in PP values from the same site. In other words, the background concentrations of PP in the cyclonic region is nearly two-fold those for both the frontal water off the Antalya bay and the Cilician basin whereas the means of POC and PON being comparable (Table 1). The average concentrations ranged regionally and seasonally between 1.44 and 3.9 μM for POC, 0.12 and 0.41 μM for PON, and 0.011 and 0.037 μM for PP in 1991-1994. The greatest mean values were estimated in the frontal waters off Antalya Bay in March 1992. However, in July 1993 and March 1994, when vertical mixing was limited and the surface water being poor in dissolved inorganic nutrients, the maximum POC's appeared in the Rhodes region where the nutricline was located immediately below the euphotic zone. In October 1991, the POC concentration was relatively high in the Cilician anticyclonic region due to as yet undefined factors.

Table 1. Average POM concentrations (μM) in the NE Mediterranean

Rhodes Cyclone

DATE	POC	PON	PP
Oct. 1991	1.55±1.48	0.13±0.06	-
March 1992	2.15±1.20	0.16±0.06	0.020±0.002
July 1993	3.07±2.52	0.26±0.21	0.020±0.01
March 1994	3.70±1.23	0.41±0.19	0.033±0.01

Cilician Basin

DATE	POC	PON	PP
Oct. 1991	2.8±1.71	0.16±0.03	-
March 1992	1.8±0.62	0.16±0.08	-
July 1993	2.7±0.82	0.29±0.21	0.015±0.01
March 1994	-	-	-

Off Antalya Bay

DATE	POC	PON	PP
Oct. 1991	1.44±0.51	0.12±0.04	-
March 1992	3.90±1.43	0.29±0.10	0.037±0.02
July 1993	2.40±1.0	0.21±0.13	0.011±0.004
March 1994	3.45±1.1	0.35±0.16	0.034±0.005

3.4.5. Ratios

Fig. 5 displays the vertical variation of the stoichiometric ratios of C, N and P in the bulk seston collected from different depths and locations. Not unexpectedly, the highest C:N ratios (16-36) appeared in October 1991 in the surface mixed layer having very low CHL but higher POC values. In March of 1992 and 1994, and July 1993 the C:N ratio generally varied between 6 and 24 over the euphotic zone; the ratio apparently decreased below 50-60 m of the Cilician basin whereas the vertical variation of particulate ratios being much less pronounced in the Rhodes cyclonic eddy. The particulate ratios from the frontal waters indicated relatively high variation with both depth and season; the C:P and N:P ratios were in the range of 180-340 and 13-21 respectively, in the surface mixed layer. These ratios decreased steadily towards the base of the euphotic zone, indicating faster decay of P-associated organic compounds in the surface mixed layer having very low CHL during summer-autumn period (Fig. 6).

Fig. 6 shows that spatial and seasonal changes in POC:CHL ratio is much greater than in the elemental composition (C:N:P ratios) of the bulk seston. The lowest and vertically almost uniform POC:CHL ratios were recorded in March-92; the ratio was as low as 35 in the cyclonic eddy and in frontal waters, whereas it slightly exceeded 100 in the Cilician basin (Fig. 6). Surprisingly, it exceeded 150-300 in March 1994, especially in the upper 30 m of the euphotic zone of cyclonic and frontal sites. Not unexpectedly, the POC:CHL ratio much increased in less productive summer period. For instance, in October 1991, it was abnormally high, varying between 100 in the cyclone, 2600 in the Cilician basin. Therefore, such large ratios were not depicted in Fig. 6. However, in July-93, the ratio appeared to decrease to levels of 800 in the mixed layer and then to 50 in the lower depths of the euphotic zone .

3.4.6. Regression of particulate data

Correlations between particulate data sets (POC, PON and PP) in pairs were examined by applying linear regression analysis. The equations given in Table 2 permit us to estimate molar ratios of C:N:P in the bulk seston during the less and more productive seasons. It appears from the Table that particulate carbon and nutrients (N, P) were highly correlated. However, the correlation coefficients for POC-PP and PON-PP regressions are lower than for the POC-PON regression. The C:N ratio derived from the slope of C-N regression was 9.85 for October 1991, which was apparently higher than the ratios of oceanic plankton (6.7) [34], of the July 1993 (7.2) and of the March 1994 (6.0) but very similar to the March 1992 ratio (9.9). The C:P ratio of the seston was also variable, ranging from 107 in March 1992 to 123 in July 1993. Interestingly, the temporal variation of C:P ratio was less than in the C:N ratio of the bulk seston. The C:P ratios of July 1993 and March 1994 are very similar and higher than an estimate of 107 for March 1992 when the surface water was relatively enriched with dissolved inorganic nutrients by the supply from deep waters (see Fig. 4). The N:P ratio of the bulk seston from the nutrient poor surface waters of NE Mediterranean was estimated to be 16.4 and 17.3 for March 1994 and July 1993, respectively. They are very similar to the planktonic ratio of 16 [34]. Unexpectedly, the N:P ratio was anomalously low (11) in March 1992.

Table 2. Linear regression analysis for organic carbon, nitrogen and phosphorus in seston from the euphotic zone of the NE Mediterranean

Date	Regression	r^2	n	Significance level
Oct. 1991	C=9.85±2.97N+0.26±0.44	0.50	15	p<0.01
March 1992	C=9.9±3.81N+0.30±0.19 C=107±15.7P+0.04±0.43 N=11±1.36P-0.03±0.04	0.93 0.75 0.79	21 17 17	p<0.001 p<0.001 p<0.001
July 1993	C=7.2±0.43N+0.79±0.14 C=123±22.3P+0.49±0.36 N=17.3±2.2P-0.04±0.04	0.87 0.48 0.51	43 39 39	p<0.001 p<0.001 p<0.001
March 1994	C=6.0±1.09N+1.28±0.41 C=118±21P-0.74±0.74 N=16±3.8P-0.22±0.13	0.79 0.80 0.70	10 10 10	p<0.001 p<0.001 p<0.003

3.4.7. Deep Chlorophyll-a Maximum (DCM)

The formation, maintenance and location of the DCM in the water column are controlled by light attenuation and nutrient availability in the NE Mediterranean as in other seas [35, 36]. The DCM is formed at depths where the light intensity decreases to 0.5-5% of its surface value; in general, it appears at the base of the euphotic zone in the NE Mediterranean [5]. The depth of the DCM fluctuated seasonally from 45 m in the cyclonic region and 100 m in the anticyclonic region during less productive summer-autumn seasons [5]. The eddy fields also affected the depth of the DCM and, thus of the particulate maxima which were located at relatively shallower depths in the cyclonic Rhodes eddy and in the fronts+peripheries. These characteristic features appeared at the base of the euphotic zone in the anticyclonic Cilician region (Figs.5a-c and 6).

In the Rhodes cyclonic region, the depth of the nutricline determines both the thickness of the euphotic zone and the location of DCM throughout most of the year (Fig. 4). The upward diffusion of nutrients was possibly combined with the accumulation of sinking phytoplankton in the lower depth of the euphotic zone, resulting in the establishment and maintenance of the DCM with relatively high CHL-a concentrations, as previously suggested [37] for similar environments. During the cooler winter of 1992, the unusually deep convective mixing all over the NE Mediterranean resulted in relatively high nitrate-based new production estimated using Deep Chlorophyll Maximum method [38] and thus high primary production and very high f-ratio for March 1992 [33].

There appears to be a close correlation between the POM and CHL-a profiles (Figs.5a-c and 6). Apparent increases in the POM concentration at the DCM depths indicate a greater algal biomass within light-limited depth of euphotic zone than in the surface waters. Nevertheless, the co-variance of zooplankton+bacteria+detritus with phytoplankton is very likely to bias the planktonic biomass high. The coincidence of the maxima of POM with CHL generally occurred in the cyclonic eddy and its peripheries, where the pycnocline (thus the nutricline) was situated near the base of the euphotic zone. However, under severe winter conditions, the occurrence of DCM and POM peaks is prevented by intense convective mixing, as occurred in March 1992. A similar hydrodynamic feature was recorded previously in the Southeastern Mediterranean [11].

4. DISCUSSION

4.1. VERTICAL DISTRIBUTION OF POM

The abundance and vertical distribution of bulk POM in the euphotic zone of the NE Mediterranean appeared to vary by 2-3 times with season and region. The extent of such changes is determined by relative importance of complicated abiotic and biotic processes in the organic carbon and nutrient cycles in the upper layer of the marine ecosystem. In fact, the eastern Mediterranean is a typical region of low productivity and thus of low seston concentration [6, 9, 39] due to limited nutrient supply to the euphotic zone. Relatively low concentrations of POC, ranging between 2 and 5.5 μM in the open sea throughout the year, corroborates the above statement. The average POC's given in Table 1 are comparable to measurements from the Equatorial Pacific [17], from the Southeastern Mediterranean shelf water [9], from open waters of Japan and East China Seas [18] and from the Sargasso Sea near Bermuda [19].

In October 1991, when the nutrient-poor euphotic zone was seasonally stratified and had very low CHL, the surface mixed layer of the Cilician basin was relatively rich in POC compared to that of the cyclonic eddy, leading to anomalously high POC:CHL ratios (100-2600). Such large values (not shown in Fig. 6), indicate detritus-dominated POM pool in the euphotic zone over the greater part of the basin. However, the POC profile increased below the seasonal thermocline in the cyclonic Rhodes region where the nutricline is always situated near the 1% light depth throughout most of the year. This feature admits nutrient influx to the light-limited zone, leading to shade-adapted algal growth in this eddy and its peripheries. Algae in this zone sythesize more pigment relative to organic production [35, 40, 41]. Therefore, POC profiles displayed a less pronounced subsurface POC peak compared to that of the CHL-a (Figs. 5a and 6). Nevertheless, the POC:CHL ratios (60-242) estimated from the measured values within the DCM depths of the eddy were much higher than the cellular Carbon:CHL ratios determined for the light-limited depths of the oligotrophic seas [16, 17, 42], accounting for about 50 % of the total POC measured. In other words, the subsurface POC peak observed in the Rhodes cyclone was most probably dominated together by detritus+bacteria+zooplankton produced *in situ* and by biogenic particles sinking from the upper layer to the top of density gradient zone.

In March 1992, when the water column was well mixed and relatively enriched with nutrients, the lowest POC concentrations were obtained in the cyclonic Rhodes region (Table 1 and Fig. 5a) because strong convective mixing and horizontal flows in the upper layer much exceed the successive growth of algae and thus accumulation of living and non-living seston in the euphotic zone of the cyclonic eddy, other than vertically migrating planktonic species. This physical pressure also modified the characteristic subsurface POM peaks formed quasi-permanently over the basin. Accordingly, the characteristic subsurface maxima of POM appeared in the frontal waters off the Antalya Bay and Cilician basin but not in the cyclonic eddy (Fig. 5a-c). In the front, the POM peak well coincided with the depth of the maximum algal growth rate [33] observed at 10-15 % light depths whereas the CHL distribution being almost homogenous in the well-mixed euphotic zone. The maintenance of the POM peak in the frontal waters may have originated from local increases mainly of zooplankton biomass and partially of detritus+bacteria concentrations. A similar mechanism was previously suggested for the occurrence of subsurface POM peaks in the frontal regions of the Western Mediterranean Sea [43]. In February 1989, the convective mixing was strong enough to mix the water column thoroughly down to 500-600 m in the anticyclonic eddy of the southeastern Mediterranean, resulting in vertically uniform CHL profiles extending far below the photic zone [11]. Unfortunately they had measured neither the bulk seston nor biomass to understand the POM distribution in the photic zone under severe winter conditions. Interestingly, the March-92 CHL-a profile displayed a small subsurface maximum (DCM) at 50 m in the frontal waters, where the particulate concentrations decreased markedly. The maintenance of this weak CHL peak in the well-mixed water column was most probably originated from less grazing pressure on algal biomass produced *in-situ* (with relatively low POC:CHL ratio) in the light-limited zone. However, in March 1994, when the convective mixing was relatively weak and confined to the upper 100 m, the POC and PON peaks were coincident with the relatively broad CHL maximum established between 40-80 m, indicating the algal growth rate to exceed the dilution of the biomass by vertical and horizontal mixing.

The seasonal thermocline developed below the surface mixed layer prevents the nutrient supply to the photic zone from the lower layer of the open sea by vertical mixing. Therefore, in the period of spring-autumn, POM pool in the euphotic zone is principally sustained by the regenerated production, especially in anticyclonic regions where the nutricline is established much below the photic zone. A supplementary conclusion was reached by the observation of the total POC measured in the euphotic zone of the Sargasso Sea was mainly composed of detritus and algal carbon merely made up 10 % of POC [44], assuming a cellular-C:CHL ratio (w/w) of 50 [15]. It should be noted that the bulk seston retained on filters may have contained a considerable quantity of bacteria, depending on sampling depth, location and season because a substantial fraction (50%, on average) of bacteria was recorded to be collected on precombusted GF/F filter pads [45]. On the other hand, the contribution of bacterial carbon may be similar or higher than algal carbon in the oligotrophic seas [44]. This finding strongly suggest that bacterial carbon may constitute from <10% to few 10% of the total POC measured in the euphotic zone of the Levantine basin. Unfortunately no data of total bacteria biomass was available for confirming the considerable contribution of bacteria to the suspended POC pool in the NE Mediterranean upper layer during the less productive seasons. Nevertheless, bacterial carbon may account for a substantial fraction of the POC pool just below 1% light depth [44]. Thus the apparent decrease in the C:N ratio determined in the lower depths of the euphotic zone of the Levantine basin may have been originated partly from the bacterial biomass with relatively low C:N ratios and to some extent from ultraplankton growing in the light-limited zone.

4.2. REGRESSION ANALYSIS OF PARTICULATE DATA

The stoichiometry of C, N and P in the bulk seston, derived from the slopes of the linear regressions of particulate data given Table 2, are generally comparable to the Redfield C:N:P ratios of 106:16:1. Nevertheless, the C:N and N:P ratios of the March-92 seston (9.9 and 11, respectively) markedly differ from the Redfield ratio whereas the C:P ratios being very similar. In other words, when the surface waters of NE Mediterranean received sufficient nitrate from deep waters with relatively high N:P ratios (>25) [4], successive algal growth proceeded with apparently low N:P and high C:N ratios compared to the Redfield ratios. Interestingly the uptake rates of C and P by algae being similar in March 1992. Such anomalous C:N and N:P ratios in the plankton-dominated seston (because POC:CHL ratio being as low as 35-175) may have originated in either relatively low uptake rate of nitrate by photoautotrophs or faster decay of nitrogenous organic compounds in the marine ecosystem under physical stresses. Similar anomalous ratios were previously reported for the north Atlantic bloom [46, 47], and for the western coastal area of France [48], and they were attributed to the uptake of more dissolved organic and inorganic carbon constituents relative to nitrogenous constituents by phytoplankton.

Interestingly, changes in the abundance of the bulk seston occurred with an N:P ratio of 16.4-17.3 in the nutrient-poor surface waters of March 1994 and July 1993 periods (see the regressions slope in Table 2). These values are very similar to the conventional planktonic ratio of 16 [34]. This strongly suggests that the uptake of dissolved inorganic nutrients by phytoplankton and decomposition of organic nutrients in POM by bacteria proceeded at similar rates even though the chemical data from the eastern Mediterranean imply phosphorus-limited algal growth. Relatively high C:N ratios in summer-autumn period, when the surface waters were poor in both algal biomass and dissolved inorganic nutrients, were most probably the result of slower decay rate of carbohydrates in suspended organic matter [14].

The intercept of linear regressions of POC vs PON or PP from productive surface waters of the seas could imply the concentration of carbonaceous compounds that do not vary with N- and P-associated organic compounds [14]. The concentration of carbonaceous compounds is very likely to account for a remarkable fraction of the measured POC when the total stock of bulk seston decreases markedly in the euphotic zone. A close correlation was also observed between the magnitudes of intercept and nitrate deficiency in the surface water; a low intercept value is very likely when nutrient concentrations are sufficient not to limit algal growth [14]. Lab-scale studies

revealed that the protein content of POM tends to decrease as nitrate became exhausted and carbohydrates and lipids to increase whilst the slope of the regression line was affected slightly [49]. Inspection of the regressions equations in Table 2 indicate that the intercept of POC vs PON regression was relatively low (10 % of POC in Table 1) in March 1992 when the nutrients were not a limiting factor for algal growth, confirming the above suggestion. The intercept, as an index of carbohydrate concentration in POM being low in the euphotic zone, increased apparently in July 1993 and March 1994 when the photic zone was relatively poor in nutrients. Estimates of carbohydrates accounted for about 30 and 36 % of the average POC's for July 1993 and March 1994, respectively. Interestingly, as shown in Table 2, the October-91 intercept of the POC-PON regression line with the apparently high slope (9.85) was relatively low (0.26) although the surface waters being very poor in both algal biomass and dissolved inorganic nutrients. The low intercept strongly suggest that the ratio of carbohydrate to total POC remained almost constant with the increasing concentrations of POM in the euphotic zone.

4.3. POC RELATION ON CHLOROPHYLL

The POC content of bulk seston retained on filters includes both living (phyto- and zoo-plankton, bacteria) and nonliving (detritus) organic compounds. Therefore an estimate of algal-C:CHL ratio from the slope of POC-CHL regression is likely biased high whereas the magnitude of pigment-free organic compounds in the bulk seston from the intercept of linear regression may be underestimated if the other components of seston co-vary with the phytoplankton [15]. Therefore, cellular-C:CHL ratios, derived from linear regression of POC on CHL for the NE Mediterranean phytoplankton (Table 3), may have been overestimated either slightly during the bloom period or markedly during the post-bloom period. Consequently, an estimate of phytoplankton biomass from the seasonally varying but vertically invariant C:CHL ratios (the slope of POC vs CHL regression) should be used cautiously in determining the contribution of algal carbon to the POC pool in the euphotic zone of the NE Mediterranean.

Estimates of the POC:CHL ratio appeared to vary seasonally between 45 and 201 for the Levantine euphotic zone (see Table 3). The slopes of the regressions for July 1993 and March 1994 also revealed that the ratio of the DCM zone was apparently higher than the slope of the combined euphotic zone data (see Table 3). Unexpectedly, the regression line of the data from the July-93 light-limited zone and the March-94 euphotic zone had a negative intercept (Table 3). A relatively high ratio and a negative intercept are very likely to appear in the POC-CHL regression when increases in POC much exceed that in CHL from different locations or depths where the POCs reach peak values (see Fig. 2 in [15]).

Table 3: Regression analysis of POC vs CHL-a in phytoplankton populations in the NE Mediterranean

Date	Regression Analysis	r^2	n
Oct.91	not healthy	-	-
Mar.92	POC=45CHLa+15	0.50	27
Jul.93	POC=57CHLa+16	0.57	45
	*POC=91CHLa-9	0.69	10
Mar.94	POC=201CHLa-20	0.66	15
	*POC=242CHL-38	0.99	5
Jul.93+Mar.92	POC=42CHLa+16	0.50	67
Oct.91+Jul.93+Mar.94	*POC=60CHLa+15	0.50	49

* data only from the DCM zone including depths of the gradients.

Interestingly the July-93 ratio (57) was merely 25% higher than an estimate of 45 for March 1992 although the March-92 POC:CHL ratios calculated from the measured POC and CHL values at a given depth (Fig. 6) were much lower than in July 1993. The ratios derived from the regressions are not much different from the cellular C:CHL ratios in the mixed layer of other seas [16, 35, 42, 50]. These findings strongly suggest that POM increases over the euphotic zone in July 1993 and March 1992 predominantly determined by the changes in the phytoplankton biomass whereas the heterotrophic+detrital+bacteria carbon (TC) concentration varied independently of the planktonic biomass. However, a contrary view appeared in the regression analysis of March-94 data and measurements within the limited DCM zone in July 1993 and March 1994 (see Table 3). Relatively high POC:CHL ratios estimated from the regressions indicated the TC values co-varied with the algal biomass and predominated the total POC measured in the water column of the euphotic zone.

In October 1991, the POC distribution was almost vertically uniform and relatively high in the surface mixed layer of the periphery and anticyclonic region indicating the detrital material to dominate the POC pool in this nutrient-poor layer. Abnormally high POC:CHL-a ratios in October 1991 represent relatively slow growth rates imposed by nutrient limitation [35]. A similar conclusion for March 1994 period, representing a post-bloom period when CHL concentrations were very low in the nutrient depleted euphotic zone and comparable to the summer-autumn concentrations (Figs. 5a-c and 6).

The ratio estimated from the combined March-92 and July-93 data (including DCM measurements) was as low as 42 for the euphotic zone, apparently lower than a ratio of 60 derived from combined DCM data of 1991-1994. In other words, changes in the bulk seston content of the euphotic zone in March 1992 and July 1993 may have predominantly originated from planktonic biomass and partly from TC with the chemical composition given in Table 2.

Previous studies have shown that the cellular-C:CHL ratio becomes relatively high when algal growth proceeds under light-saturated and nutrient limited conditions; but it decreases markedly in the light-limited depths of the euphotic zone [35, 50]. Moreover, an estimate of algal biomass from the C:CHL ratio derived from the slope of POC-CHL regression is likely to be overestimated due to the possibility of co-variance

of TC with the algal biomass [15]. Disregarding such biasing factors, the relatively low POC:CHL ratios estimated for March 1992 and July 1993 indicate that algal carbon accounted for about 10 and 30 % of the average POCs given in Table 1 for these periods, respectively. These values were most probably overestimated to some extent when the lower ratios calculated from cell counts and carbon content of the algal cells [16, 35, 42]. They have also suggested that in the oligotrophic Sargasso Sea the growth rate of phytoplankton must be fast enough to provide sufficient organic carbon for bacterial growth, leading to very high POC:CHL ratio in the bulk seston predominantly composed of detritus and about 10% of algal carbon. A similar conclusion was reached by the estimation of merely 25% of POC measured in the Sargasso Sea in August is provided by bacterial+phytoplankton biomass [19].

5. CONCLUSIONS

During the spring-autumn period, when dissolved inorganic nutrients become depleted in the seasonally stratified euphotic zone, phytoplankton biomass is substantially low. Thus, the total of detritus+zooplankton+bacteria dominates the suspended POC pool in the NE Mediterranean upper layer as in other oligotrophic seas [19]. Nevertheless, a close correlation appears between POM and CHL profiles in the cyclonic Rhodes region and its peripheries because the nutricline is always situated near the base of the euphotic zone throughout most of the year. In these sites, the subsurface particulate maxima appear to be consistent with the DCM. The elemental composition (C:N:P ratios) of the bulk seston derived from the regression analysis of particulate data is generally comparable with the Redfield 106:16:1 ratios. However, the C:N ratio of the bulk seston apparently decreases below the seasonal thermocline where irradiance becomes a limiting factor for algal growth. This indicates the suspended organic matter existing in the light-limited deep euphotic zone to be mostly produced *in situ*, rather than the particles sinking from the nutrient-limited surface layer.

Anomalously low N:P ratios (6-12) of the bulk seston appeared in the March 1992, when the euphotic zone was enriched with dissolved inorganic nutrients (and relatively high N:P ratio) and much productive. Such low N:P ratio of the bulk seston strongly suggests that POM is exported to the lower depths with much lower N:P ratios than that of nitrate to reactive phosphate (26-28) in the Levantine deep water (LDW). The profound conflict between the elemental composition of POM produced during spring bloom and nitrate to phosphate (N:P) ratios in the LDW and LIW has led to propose another source for anomalously high nitrate to phosphate ratios observed in such water masses and it has been suggested that both the LDW and LIW had originally very high ratios of biologically labile nitrogen to phosphorus before its sinking to the deep basin during the winter mixing [4]. Relatively fast release of nitrogenous organic compounds from POM of planktonic origin increase DON content of the surface waters during late-winter bloom as observed in the productive waters [51]. They then sink with relatively high concentrations of biologically labile organic nitrogen, yielding higher N:P ratio in the aged intermediate and deep water masses. Nevertheless, this suggestion should be supported by late winter measurements at the origins of LDW and LIW.

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